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Publication date:
2018

Document Version
Publisher's PDF, also known as Version of record

DTU Chemical Engineering
Department of Chemical and Biochemical Engineering

Reactivity of sewage sludge, RDF, and straw chars towards NO

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Introduction - Minimizing NO_X emissions from solid fuel combustion is important due to the harmful environmental impact and strict emission regulations. While the gaseous chemistry of nitrogen is fairly well established, the heterogeneous reduction of NO by char is less understood. This study investigated the reduction of NO over sewage sludge, RDF, and straw chars in a fixed bed reactor at varying temperatures and NO inlet concentrations.

Background - Conversion of char-N to NO

- Increasing importance of waste fuels – lower fuel cost and avoid landfilling.
- NO_X in post-combustion effluent primarily in the form of NO.
- Emission of NO from char combustion determined by competing NO formation (R1,R2) and reduction (R3-R9) reactions in boiler (Chambrion et al. 1998, Karlström et al. 2017).
  - M = (Ca, Fe, K, Mg, Na)
  - (-X) = surface complex

O_2 + (-C) + (-CN)	→	(-CO) + (-CNO)	(R1)
(-CNO)	→	NO + (-C)	(R2)
NO + 2 (-C)	→	(-CO) + (-CN)	(R3)
2 (-CN)	→	N_2 + 2 (-C)	(R4)
(-CN) + NO	→	N_2 + (-CO)	(R5)
2 NO + 2 CO	→	N_2 + 2 CO_2	(R6)
($-M_XO_Y$) + (-C) + NO	→	($-M_XO_{Y+1}$) + (-CN)	(R7)
($-M_XO_{Y+1}$) + (-C)	→	($-M_XO_Y$) + (-CO)	(R8)
(-CO)	→	CO + (-C)	(R9)

Materials and methods

- Char preparation
  - Demineralization
  - Pyrolysis
  - Sieving


Straw (S)


Refuse Derived Fuel (RDF)

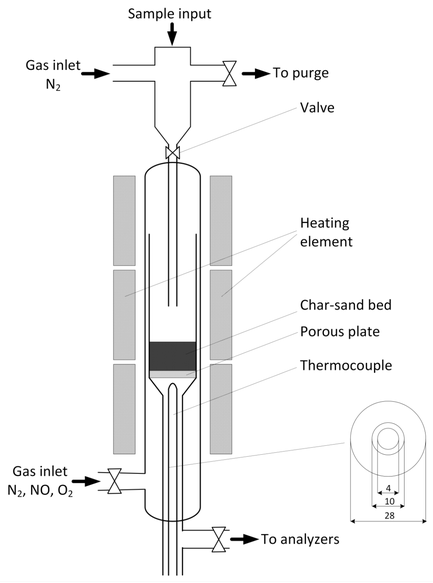

Sewage Sludge (SSL)


800°C (10min)


HNO_3 (pH 2) 800°C (10min)

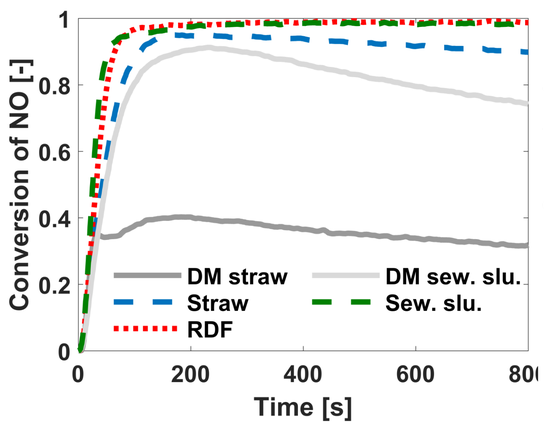

Raw and demineralized chars (125-180µm)

- Fixed bed char combustion
  - 10% O_2/N_2
  - 800°C
- Fixed bed NO reduction by char
  - [400,800,1500] ppmv NO//N_2
  - [800,850,900] °C

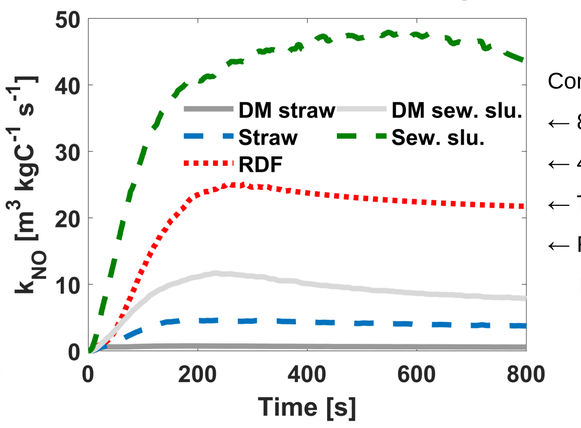


Results

1. Reduction of NO

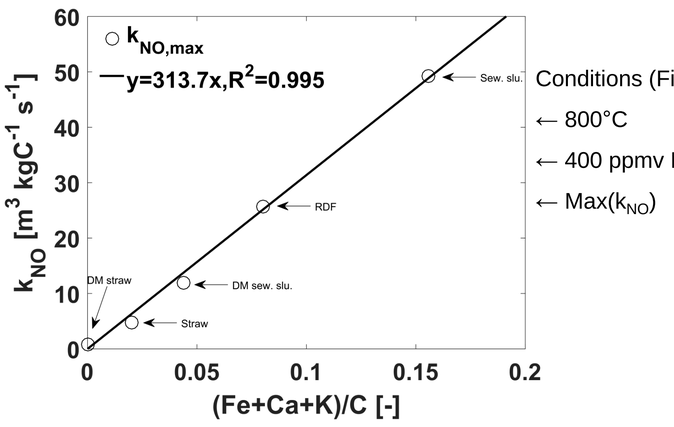


2. First order reactivity



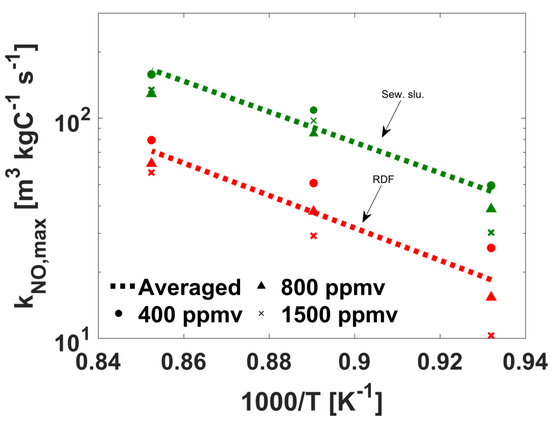
Conditions (Fig.1,2)
← 800°C
← 400 ppmv NO
← Total flow 1 NL/min
← Reduction rate: $R_{NO}=k_{NO}\,C_{NO}$

3. Influence of ash forming elements

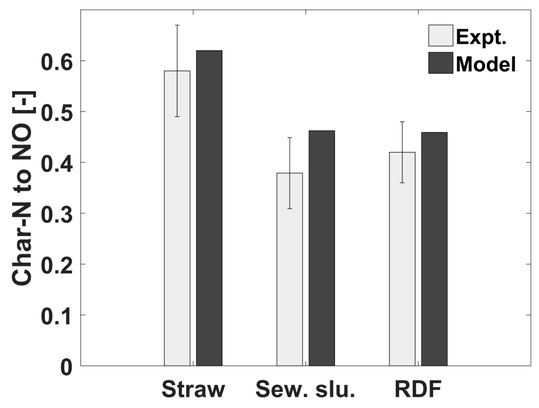


Conditions (Fig. 3)
← 800°C
← 400 ppmv NO
← Max(k_{NO})

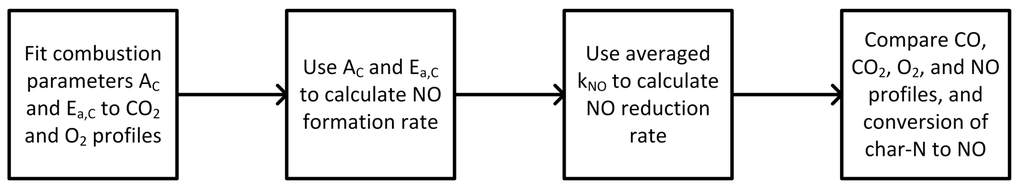
4. Averaged first order reactivity



5. Conversion of char-N to NO



- 1D heterogeneous, transient, non-isothermal packed bed reactor model + one-parameter description of flue gas mixing.
- NO formation (R1-R2) proportional to combustion rate with N/C as proportionality constant.
- Char-N to NO and N_2O determined by FTIR measurements of combustion experiments.
- Non-convex optimization problem i.e. strongly dependent on initial guess



Char	A [m^3 kgC^{-1} s^{-1}]	Ea [kJ/mol]
Straw	$3.91 \cdot 10^7$	145
Sewage sludge	$1.39 \cdot 10^8$	133
Refuse derived fuel	$1.35 \cdot 10^8$	141

- Recommended kinetic parameters for the modelling of NO-char interaction for RDF, sewage sludge, and straw chars

Conclusions

- Sewage sludge and RDF chars exhibited a high reactivity towards NO reduction
- The initial NO reduction reactivity correlated well with the (Ca+Fe+K)/C molar ratio in the unreacted chars.
- A simple mathematical model based on first order kinetics described the conversion of char-N to NO in fixed bed combustion reasonably well.
- The obtained kinetic parameters could be implemented in large scale simulations.

Future work

- Investigate the influence of O_2 and CO on the reduction reactivity of waste fuel chars.
- Examine possibilities of using waste chars as primary or secondary measures for NO_X minimization, e.g. additive in the cyclone.

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